Development and field validation of an indicator to assess the relative mobility and risk of pesticides in the Lourens River catchment, South Africa.

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Abstract

A GIS based pesticide risk indicator that integrates exposure variables (i.e. pesticide application, geographic, physicochemical and crop data) and toxicity endpoints (using species sensitivity distributions) was developed to estimate the Predicted Relative Exposure (PREX) and Predicted Relative Risk (PRRI) of applied pesticides to aquatic ecosystem health in the Lourens River catchment, Western Cape, South Africa. Samples were collected weekly at five sites from the beginning of the spraying season (October) till the beginning of the rainy season (April) and were semi quantitatively analysed for relevant pesticides applied according to the local farmers spraying programme. Monitoring data indicate that physicochemical data obtained from international databases are reliable indicators of pesticide behaviour in the Western Cape of South Africa. Sensitivity analysis identified $K_{oc}$ as the most important parameter influencing predictions of pesticide loading derived from runoff. A comparison to monitoring data showed that the PREX successfully identified hotspot sites, gave a reasonable estimation of the relative contamination potential of different pesticides at a site and identified important routes of exposure (i.e. runoff or spray drift) of different pesticides at different sites. All pesticides detected during a monitored runoff event, were indicated as being more associated with runoff than spray drift by the PREX. The PRRI identified azinphos-methyl and chlorpyrifos as high risk pesticides towards the aquatic ecosystem. These results contribute to providing increased confidence in the use of risk indicator applications and, in particular, could lead to improved utilisation of limited resources for monitoring and management in resource constrained countries.

**Keywords:** pesticides; risk indicator; validation; Lourens River; South Africa
1. Introduction

Nonpoint source agricultural pollution is generally considered one of the major threats to surface water quality in rural areas (Loague et al., 1998). Nutrients, sediments and pesticides potentially enter aquatic environments via runoff, leaching and spray drift and pose a risk to the communities that inhabit them. Of all nonpoint source pollutants, insecticides are among the most crucial chemical stressors, simply because of their extremely high toxicity to many non-target aquatic organisms (fish and macroinvertebrates). Only a few studies have investigated the occurrence and effects of current-use pesticides in South Africa. The most extensive research has been performed in the Lourens River, in the Western Cape of South Africa. Studies have shown that current-use insecticides frequently enter the river via runoff and spray drift (Schulz, 2001a; Schulz, 2001b; Dabrowski and Schulz, 2003). Although contamination is transient, field, experimental microcosm (Schulz et al., 2002) and in-situ bioassay studies (Schulz, 2003) have shown that measured pesticide levels pose significant risks to aquatic macroinvertebrate communities in the Lourens River. Another study measured high levels of chlorpyrifos and endosulfan in a number of agricultural catchments throughout the Western Cape (London et al., 2000).

Despite these findings, the potential impact of pesticides in South African surface waters has generally been a low priority and is generally not considered in aspects of water resource management, especially with regards to routine monitoring. Even in developed countries, despite strict regulatory procedures, pesticides are frequently detected in surface waters at concentrations that exceed environmentally acceptable levels (Stehle et al., 2012). Although intensive monitoring and sampling can identify pesticide impacts, the cost of analysis and logistics makes this a highly costly exercise (particularly in the context of less developed countries). Thus there is a need to develop cost effective methods of predicting the environmental risks of pesticide use on a catchment specific basis which can be used to prioritize specific pesticides for monitoring purposes and identify spatial
patterns of contamination. Environmental pesticide risk indicators provide a relative indication of the impact of pesticides (Levitan et al., 1995), with an emphasis on relatively few and simple data input parameters (Kookana et al., 2005). Risk indicators vary greatly in terms of their purpose, and methodology and are often very broad in scope covering, for example, the impact on aquatic organisms, soil organisms, bees, occupational exposure and human health effects (Reus et al., 2002). With respect to aquatic ecosystems, risk indicators are generally regarded as lower tier risk assessment tools that provide a relative assessment of the environmental impact of pesticides through integration of multiple catchment-scale factors that influence the fate, transport and toxicity of pesticides. These include site specific geographical conditions (e.g. soil type, soil organic matter content, water input, slope of land, soil loss, recharge rate, depth of water table etc), ecotoxicological (e.g. LC$_{50}$ data or species sensitivity distributions) and environmental fate (e.g. half-life and $K_{OC}$ values) properties and pesticide use data (Sánchez-Bayo et al., 2002; Sala and Vighi, 2008). On a first level of assessment, risk indicators may be designed to prioritise pesticides in terms of their anticipated risk towards the aquatic environment (Kookana et al., 2005). Integration of GIS may enable the identification of potential trouble spots and vulnerable areas where risk reduction might be requisite (Pollock et al., 2005). Furthermore, risk indicators can potentially highlight the most important route of contamination of surface waters (i.e. via runoff during rainfall or spray drift during pesticide application) and therefore provide valuable insight with respect to risk mitigation strategies for certain pesticides (Huber et al., 2000; Verro et al., 2002). Risk indicators are therefore attractive alternatives to expensive, intensive monitoring campaigns or more data intensive mechanistic models. Given these attributes, risk indicators may be particularly beneficial to developing countries, where the costs of monitoring are prohibitive and data requirements are lacking or difficult to obtain.

While a number of indicator methodologies have been developed, very few studies have attempted to validate the outputs of the indicators. This is particularly relevant in more arid countries such as South Africa which often make use of physicochemical data derived in northern temperate countries for exposure assessment predictions (Dabrowski and Schulz, 2003). The paper describes the development
and validation of a risk indicator designed to assess the relative potential exposure and risk of pesticides in agricultural surface waters. The objective of the indicator is to provide a relative, qualitative measure of pesticide mobility and associated risk to aquatic organisms and not exact quantitative measures of risk. The tool integrates ecotoxicological effect data and exposure indicators using empirical modelling and GIS techniques to a.) identify high priority pesticides in a catchment in terms of their mobility and potential toxicological effects b.) identify high risk areas (or hotspots) within a catchment where pesticide inputs are unacceptably high and c.) characterise the most important route of transport (i.e. runoff or spray drift). Results of the mobility indicator are compared to field monitoring data in an attempt to validate predictions made by the indicator.

2. Materials and Methods

2.1 Study Area

The Lourens River rises at an altitude of 1080 m in a naturally vegetated fynbos (part of the Cape floral kingdom, endemic to South Africa) area and flows in a south-westerly direction for 20 km before discharging into False Bay at the Strand (S34°06´; E18°48´). The catchment region is characterised by intensive farming, with orchards and vineyards in its middle reaches. The Lourens River has a total catchment area of 92 km² and receives an annual mean rainfall of 915 mm, most of which falls during the autumn, winter and early spring months between April and October, as is characteristic of the region’s Mediterranean climate. The main soil type is silty loam and the slopes in the catchment vary between < 2 % in the area near the river and < 8 % in the upstream stretches of the river and some of the tributaries. Apples, grapes (for wine production), pears and plums are grown in the area, to which a number of insecticides and fungicides are applied on an annual basis, mainly between August and February of the following year. Previous studies in this catchment have shown runoff and spray drift to be important routes of entry into tributaries of the Lourens River (Schulz, 2001a; Dabrowski and Schulz, 2003).
Five sites were selected for monitoring and validation purposes. One site was located in the Lourens River main stem (LR) and was representative of the entire catchment (Fig. 1). Four additional sampling sites, (named after the orchard in closest proximity to the site - BB7, LG4, C and VW) were located within four tributaries flowing into the Lourens River. Each of the four tributaries are characterised by different crops, buffer zone distances and slope categories (Fig. 1). The catchment area of each of the tributaries was delineated using GIS. This allowed for the characterisation of geographical attributes and the quantification of crop coverage (and associated pesticide use) within the sub-catchments.

2.2 General Approach

The indicator involves four distinct steps. First, pesticide application was estimated for each sub-catchment based on crop area and crop specific pesticide application information. Secondly, Predicted Environmental Loads (PEL; kg) of all applied pesticides moving into the tributaries via the combination of runoff and spray drift were estimated for each sub-catchment. Thirdly, the PEL and simple hydrological characteristics of the tributaries were used to estimate predicted environmental concentrations (PECs; µg L\(^{-1}\)) for each pesticide in each sub-catchment. The PECs were expressed as a ratio of the pesticide with the highest PEC across all sub-catchments, so as to provide a predicted relative exposure (PREX) score of mobility of all pesticides across all sub-catchments included in the analysis. Finally, the PECs and relevant aquatic toxicity data were used to derive toxicity to exposure ratios (TERs) which provide an estimation of risk. The TERs were also expressed as a ratio of the pesticide with the highest TER across all sub-catchments so as to provide a predicted relative risk indicator score (PRRI) for all pesticides applied in all sub-catchments.

2.3 Pesticide Use

Pesticide application data were obtained from spray records provided by the farmers. For each sub-catchment the total amount of pesticide (kg) applied to each orchard type was estimated based on
orchard area and the rate and frequency of application. This was done for each of the four tributaries as well as for the entire catchment (Supplementary Data Table S1). Azinphos-methyl, chlorpyrifos, carbendazim, prothifos and methyl parathion are all applied in relatively high quantities. Flufenoxuron, propiconazole, beta-cyfluthrin and cypermethrin are all applied in low quantities.

2.4 Spray Drift Loads

Using GIS, distinct buffer zone distance categories (5, 7.5, 10, 15, 20, 30 and 40 m) were created for each river stretch in the catchment (assuming 40 m is the maximum distance at which contamination would occur). This process identified orchards that fell within each of the buffer distance categories. The associated buffer zone width and total pesticide application for each of these orchards were used as input to estimate the contribution of spray drift to total pesticide loads entering the adjacent tributary. No vegetated hedges were located between orchards and the tributaries. For each orchard, the total loss of active ingredient per crop type was calculated using a formula generated from drift values derived by (Rautmann et al., 1999):

\[ L_{\%spray} = \frac{1}{a + bx^2} \]

where \( a = 0.03597 \) and \( b = 0.00179 \) and \( x \) is the buffer zone width. The \( L_{\%spray} \) value and the total pesticide application per orchard were used to estimate the total loss of the active ingredient from the field during the spraying season. For each crop type, the total loss of each active ingredient was multiplied by the water index (Supplementary Data Table S2) to obtain a final loss (kg) per crop type. The water index is the probability of surface water lying adjacent to a field and is expressed as a ratio of the length of the water body \( (L_{WB}) \) lying adjacent to the field to the perimeter \( (P_{Field}) \) of the field:

\[ WI = \frac{L_{WB}}{P_{Field}} \]
The total loss of each active ingredient derived from spray drift was calculated by summing the total loss of each active ingredient from each crop type.

2.5 Runoff Loads

Only orchards directly adjacent to river reaches were included for analysis in the calculation of the proportion of pesticide loading attributed to runoff. A digital elevation model (DEM) for the catchment area was transformed into slope categories using Spatial Analyst in ArcGIS 9.3 (Fig 1). Each orchard area was over-layered with the slope profile, so as to generate a shapefile containing polygons describing crop type and the associated slope category (percentage). As some orchards covered more than one slope category, these fields were sub-divided into smaller polygons, each with its own unique slope category. It was assumed that runoff will only take place during rainfall events in excess of 10 mm (Huber et al., 2000).

Rainfall data from a weather station in the catchment was assessed over a ten year period. The average rainfall for all events exceeding the 10 mm threshold was 20 mm. The total length of the spraying season is approximately 210 days (i.e. from beginning of August to the end of February). During this period an average of ten rainfall events in excess of 10 mm are expected to occur. The rainfall interval was therefore assumed to be 20 days (i.e. one rainfall event every 20 days). Considering the rainfall interval of 20 days, a rainfall event could occur at least 0 days after a spraying event or at the most 20 days after the spraying event. Thus the median of this interval was chosen (i.e. 10 days) as the typical number of days for a rainfall event to occur after application.

For each orchard, the total loss of active ingredient per crop type was calculated using a formula by Reus et al. (1999):

\[
L_{\% \text{runoff}} = \left( \frac{Q}{P} \right) \times f \times \exp \left( -t \times \ln \frac{2}{DT50_{\text{soil}}} \right) \times 100 \left( 1 + Kd \right)
\]
where $L_{\text{runoff}}$ = percentage of application dose being available in runoff water as a dissolved substance; $Q$ = runoff amount (mm) calculated according to hydrological models (Lutz (1984) and Maniak (1992)); $P$ = precipitation amount (mm); $DT_{50_{\text{soil}}}$ = half-life of active ingredient in soil (d); $f_1 = f_1 \cdot f_2 \cdot f_3$, the correction factor reflecting the influence of slope ($f_1 = 0.02153 \cdot \text{slope} + 0.001423 \cdot \text{slope}^2$), plant interception ($PI$), the percentage of applied pesticide intercepted by trees in the orchards ($f_2 = 1 - \frac{PI}{100}$), and buffer width ($f_3 = 0.83^{WBZ}$, and $WBZ$ is the width of buffer zone [m]; if the buffer zone is not densely covered with plants, the width is set to zero); $t = \text{time (d)}$ between application and rainfall; $K_d = (K_{OC} \cdot OC\%)$, a factor reflecting the tendency of the pesticide to bind to organic carbon in the soil mL g$^{-1}$, where $K_{OC}$ is the sorption coefficient of the active ingredient to organic carbon (mL g$^{-1}$) and OC\% is the organic carbon content of the soil. The tables developed by Lutz (1984) and Maniak (1992) were used to obtain the $Q$ value corresponding to the average rainfall for events above 10 mm for this catchment (i.e. 4.93 for a rainfall event of 20 mm). The organic carbon content of the soil was assumed to be 0.75 % (AGIS, 2012). The plant interception factor was assumed to be 80 % (i.e. 80 % of the applied substance lands on the crop). A buffer width of 0 m was used as input as throughout the catchment, deep erosion rills provide a direct pathway between orchards and adjacent water bodies, thus making the effectiveness of any vegetated buffer strip negligible. Pesticide physicochemical data was obtained from the EU-Footprint database (Supplementary Data Table S3; FOOTPRINT, 2006).

The total loss of active ingredient per crop type was calculated for each orchard segment (i.e. polygon with associated orchard type and slope category), using the $L_{\text{runoff}}$ value and the total amount of pesticide applied to the orchard during the spraying season. The total loss of each pesticide per orchard was calculated and multiplied by the water index to estimate the final load derived from runoff. The total loss of each active ingredient was then calculated by summing the total loss across each crop type (i.e. for those active ingredients applied to more than one crop type). For each subcatchment the total loss of active ingredient associated with spray drift and runoff was summed to provide a final estimate of PEL.
2.6 Predicted Relative Exposure (PREX)

The PEC ($\mu$g L$^{-1}$) for each pesticide at each sub-catchment was calculated as follows:

$$PEC = \frac{PEL}{D}$$

where $D$ is the discharge of the stream in m$^3$ s$^{-1}$. This calculation does not take temporal aspects of contamination into consideration and assumes that the concentration is derived from all pesticide losses occurring simultaneously and entering the water resource simultaneously over a 24 hour period.

However, the indicator is designed to provide an estimate of the relative concentrations of a number of pesticides compared to one another and is not designed to give accurate pesticide concentrations as would be detected in the field.

The PEC for each pesticide in each sub-catchment was expressed as a ratio of the highest PEC for all pesticides included in the analysis (176.9 $\mu$g L$^{-1}$ for dimethomorph at LG4), resulting in (PREX) scores ranging from 1 downwards. This method of calculating the PREX scores ensures that the transport and concentration of the different active ingredients is expressed relative to the active ingredient with the highest PEC. The scores were used to assign an exposure category to each pesticide, namely, Very Low (0 – 0.2), Low (0.2 – 0.4), Medium (0.4 – 0.6), High (0.6 – 0.8) and Very High (0.8 - 1). This method of categorisation implies that results are specific to this study area.

However, the methodology can easily be applied to other catchments or to more than one catchment simultaneously, using the highest PEC for all pesticides across all catchments as the benchmark against which to determine PREX scores.

2.7 Predicted Relative Risk (PRRI)
The PEC for each pesticide in each sub-catchment was divided by the corresponding toxicity value to obtain the TER. SSDs were derived using BurliOz software (Campbell et al., 2000) and the concentration at which 95% of freshwater species (which included fish, invertebrates and algae) would be protected was used as the toxicity value for each active ingredient. Only LC50 data were used to derive the SSD. For some pesticides (dimethomorph, flufenoxuron, flusilazole, prothiofos, thiacloprid and trifloxystrobin), insufficient data were available to construct a SSD. In these instances the risk was calculated using LC50 value for *Daphnia magna*. Toxicity data were obtained from the USEPA EcoTox database (USEPA, 1994). Chlorpyrifos at site C had the highest TER (190.4) and all TERs for all pesticides in each sub-catchment were divided by this value to obtain the final PRRI value. The scores were used to assign a risk category to each pesticide, namely, Very Low (0–0.2), Low (0.2–0.4), Medium (0.4–0.6), High (0.6–0.8) and Very High (0.8–1).

2.8 Sensitivity Analysis

A sensitivity analysis was performed to determine the relative importance of input variables in the runoff and spray drift models used to calculate the PREX. This was performed according to the methodology presented in Dubus et al. (2003). The method of analysis is a simple approach and is referred to as one-at-a-time sensitivity analysis. This involves varying input parameters independently, one at a time, all other parameters being constant and observing the influence on model predictions. For this analysis, runoff and spray drift model input parameters were varied in increments within realistic minimum and maximum ranges (Supplementary Data Table S4).

The assessment of model sensitivity was based on the ratio of the relative variation in model output to the relative variation in model input. For each variation increment, the relative variation in model input and model output were calculated as follows:

\[
\text{Input Variation} = \frac{I - I_{BC}}{I_{BC}} \times 100
\]
Output Variation = \frac{O - O_{BC}}{O_{BC}} \times 100

where \( I \) is the value of the input parameter, \( I_{BC} \) is the value of the input parameter for the base-case scenario, \( O \) is the value of the output variable, and \( O_{BC} \) is the value of the output variable for the base-case scenario. The base-case scenario is the set of input variables that are representative of typical or average conditions (i.e. the input variables that provide a general description of the application, physicochemical and geographical characteristics – Supplementary Data Table S4). For runoff, the base-case input parameters for physicochemical properties were the median values for those properties for all pesticides applied in the Lourens River catchment. Area, slope and application rate were all defined by the median values for those parameters. Only those input parameters that varied amongst pesticides and sites were included in the sensitivity analysis. For spray drift average distance of crops to streams and median pesticide application characteristics were used for the base-case scenario (Supplementary Data Table S4).

The ratio of variation (ROV) can be defined as follows:

\[ ROV = \frac{Output\ Variation}{Input\ Variation} \]

The ratio can be either positive or negative. It takes negative values if a decrease in an input parameter results in an increase in the output value or if an increase in an input parameter results in a decrease in the output value. The sign of the ratio is not critical when the aim is to classify input parameters according to their influence on model output. An ROV of 1 means that a variation in the model input will result at maximum in the same variation in the model output. An ROV of 10 will result in a maximum variation of the output by 10 times.

2.9 Sampling Design
A field monitoring study was designed in order to attempt to validate the outcomes of the risk indicator methodology. Due to the transient nature of pesticide contamination, it is often difficult to detect pesticides using a routine sampling routine. Samples were therefore collected so as to coincide with periods when pesticide contamination of the water bodies is expected to occur. Weekly sampling was conducted during the main pesticide application period (beginning of October 2009 to end of February 2010), which is characterised by and high winds, with spray drift being the most likely route of entry for pesticides into surface waters. Occasional storm events during this period lead to high input of pesticides (Schulz 2001b). Weekly sampling commended again from the beginning of August 2010 to end of September 2010 to coincide with a high rainfall period and the start of the spraying season.

Water samples were collected in 1 L acetone-washed glass containers with a screw cap lined with clean aluminium foil. Samples were immediately placed in a cool box containing ice and kept in dark conditions. Sediment samples were collected at deposition zones at each of the sites. Sediment samples were collected from approximately the top 1 cm of deposition zones at each site using a metal scoop and were stored in 250 mL glass containers. All samples were stored at 4 degrees or below from time of collection until extraction. In addition, a runoff event (18 mm of rainfall during a one hour period) was monitored during November 2010. Samples were collected by auto-runoff samplers designed to collect samples during increased discharge according to methods described in Dabrowski et al. (2002a) and are representative of peak concentrations during runoff conditions. Water (filtered prior to analysis) and sediment samples were extracted and prepared for analysis according to methods described in Dabrowski et al. (2002a). The detection of target pesticides was performed by Hearshaw and Kinnes Analytical Laboratory using a semi-quantitative multi-residue screening analysis analysed by using liquid chromatography-mass spectrometry. All active ingredients apart from flufenoxuron were included in the screening analysis. For water samples, the limits of detection were 0.05 µg L\(^{-1}\) for carbendazim and flusilazole; 0.1 µg L\(^{-1}\) for alpha-cypermethrin, beta-cyfluthrin, chlorpyrifos, cypermethrin, endosulfan, methyl-parathion, prothiofos and trifloxystrobin; 0.5 µg L\(^{-1}\)
for carbaryl, dimethomorph and thiacloprid and 1 µg L\(^{-1}\) for azinphos-methyl and propiconazole. For sediment samples, limits of detection were 10 µg kg\(^{-1}\) for all active ingredients.

3. Results and Discussion

3.1 Measured Pesticide Exposure

Monitoring data clearly indicate that site LG4 and C are more contaminated than sites BB7 and VW (Table 1). In general the frequency of detection of pesticides for all sites was relatively low (particularly in the water phase), and only nine of the fifteen pesticides analysed for were detected. Azinphos-methyl, carbaryl, carbendazim, chlorpyrifos, dimethomorph, methyl parathion and prothiofos were most commonly detected and were also the most heavily applied pesticides in the catchment (Supplementary Data Table S1). Contamination would therefore seem to be closely linked to the overall quantity of pesticides applied in the catchment. Similarly, of the six pesticides not detected, the majority were applied in comparatively low quantities, particularly propiconazole, cyfluthrin, alpha-cypermethrin and cypermethrin. However, the fact that azinphos-methyl, carbendazim and methyl parathion were applied in similar quantities in LG4 and VW, yet were detected more commonly in the LG4 tributary, indicates that additional geographical factors influence the mobility of pesticides in the respective catchments. In this example the steeper slopes in the LG4 catchment (Fig. 1) most likely result in higher frequencies of contamination (Dabrowski et al., 2002b). The low frequency of detection and concentrations of all pesticides in the catchment is not surprising. As pesticide transport is event driven (i.e. as a result of spraying or rainfall in the catchment), environmental pesticide concentrations are often transient and generally occur in peaks for a relatively short period of time after the event (Holvoet et al., 2007). Although designing monitoring programmes to take samples during expected peak transport periods (i.e. during the spraying and runoff seasons) is likely to improve the ability to detect pesticide levels, weekly routine sampling may often miss these peaks and result in non-detectable concentrations, particularly in small catchments (Crawford, 2004; Holvoet et al., 2007). In this respect event-based runoff and spray-drift
Sampling could provide a better assessment of pesticide exposure in streams and rivers (Stehle et al., 2012). This was demonstrated by the fact that the runoff event monitored on the 15th of November showed a relatively high number of detections within the context of this study (Table 2).

Pesticides were more frequently detected in the sediment phase (75 detections across all sites), the most commonly detected being, azinphos-methyl, chlorpyrifos, prothifos and methyl parathion. Partitioning between the sediment and water phase could largely be explained by the physicochemical properties of the pesticides, particularly the $K_{OC}$ values (Supplementary Data Table S3). Pesticides with $K_{OC}$ values higher than 1000 were found almost exclusively in the sediment phase (i.e. azinphos-methyl, chlropyrifos, flusilazole, methyl parathion and prothiofos), while those below 1000 were found almost exclusively in the water phase (i.e. carbaryl and dimethomorph). Carbendazim was detected on a number of occasions in both the sediment and water phase. Data on physicochemical properties of pesticides in South Africa is not locally available and values used in this study were obtained from a European database. There is often a degree of reservation about using physicochemical data from more temperate climates as combinations of the chemical properties as well as site-specific conditions determine the fate and behaviour of pesticides (Daam and Van den Brink, 2010). These conditions vary greatly among different agro-ecological zones making the direct extrapolation of data between geographical regions very challenging (Ahmad and Kookana, 2007). However, Wauchope et al. (2002) found that while there is often variation in the $K_{OC}$ value of a specific pesticide, the values are adequate for discriminating between the relative mobility of a number of different pesticides. A study on the behaviour of three pesticides in South African soils reported similar $K_{OC}$ values to those reported in the international literature, while half-lives were generally longer in South African soils (Meinhardt, 2009). Other studies performed in South Africa have also shown good correspondence between $K_{OC}$ values and partitioning of pesticides between the sediment and water phase (Dabrowski et al., 2002b; Sereda and Meinhardt, 2005). These studies, as well as data from this study indicate that the European values provide a relatively good indication of pesticide behaviour in soils of South Africa and can be reliably used in environmental fate modeling for South African conditions.
This observation is relevant considering that the sensitivity analysis showed the $K_{OC}$ value plays an important role in estimating runoff related loads in the calculation of the PREX score (Fig. 2a). The closer the curve to the Y axis (i.e. the larger the slope of the line linking the origin and a particular point), the more sensitive the model is to this parameter. Similarly, the closer the curve to the X axis (i.e. the smaller the slope of the line linking the origin and a particular point), the less sensitive the model is to this parameter. Curves corresponding to positive influences (an increase in model output resulting from an increase in model input or a decrease in model output resulting from a decrease in model input) are located in the top right and bottom left quadrants while those corresponding to negative influences (an increase in model output resulting from a decrease in model input or a decrease in model output resulting from an increase in model input) are situated in the top left and bottom right quadrants. Thus, for runoff, the model is most sensitive to the input of $K_{OC}$ with lower values resulting in large changes in output variation. For half-life runoff output is sensitive to shorter half-lives, resulting in decreased model output (i.e. lower transport in runoff). As half-life increases it results in an increase in the model output (i.e. higher pesticide transport in runoff), however the model becomes less sensitive to this parameter at higher half-lives. For slope, variation just about or below the base-case scenario (i.e. the origin) results in almost linear response with respect to model output. However as slope increases further, the model becomes more sensitive to this particular input parameter. Application rate, frequency of application and the area of the treated crop all display a linear relationship in terms of the effect of input variation on the model output. It is also important to note that the 10 day input parameter was applied for all pesticides in all sub-catchments. In reality the time will therefore not influence the relative mobility of the different pesticides within a single catchment as this will be determined by half-life. However if two different catchments from two geographical areas were compared, then timing of the rainfall event in relation to application would be important.

For spray drift, the model is most sensitive to a decrease in distance between the point of application and the water body (Fig. 2b). As buffer zone width increases, the model becomes less sensitive and
also results in a decrease in the model output. As for runoff, application rate, frequency of application and the area of the treated crop all display a linear relationship in terms of the effect of input variation on model output. In summary, these results show that for a given pesticide $K_{OC}$ and buffer zone width have the highest influence on model predictions for runoff and spray drift, respectively.

3.2 Predicted Pesticide Exposure

Field validation of predictive indicators and models is very challenging, particularly with respect to pesticides, where a number of factors influence their transport into and fate within an aquatic resource. Detections of pesticides in water and sediment at each site were used to assess the accuracy of the indicator in predicting pesticide exposure. Dissolved pesticides can easily be incorporated into the sediment during runoff or spray drift events after entering the stream (Erstfeld, 1999; Rand, 2004). In this respect, sediment results are important in terms of validating the indicator. However, depending on the hydrology of the stream and physicochemical properties of the pesticide, repeated monitoring of sediment at a site may be representative of a single contamination event. For example prothiofos with a relatively high half-life (45 days), was detected frequently in the sediment at C and LG4. These two streams also had the lowest discharge of all streams monitored, potentially reducing the potential for contaminated sediment to be washed away. Thus, the combination of high half-life and low stream discharge could potentially result in this specific pesticide being repeatedly detected over a comparatively long period of time, resulting in a high observed frequency of detection. Finally sediment and adsorbed pesticides are physically washed into streams during heavy rainfall events, a process not covered by the indicator published here. Of the commonly applied pesticides, prothiofos had the highest $K_{OC}$ and sediment bound input is therefore a likely means of contamination.

Apart from prothifos, the mobility and occurrence of pesticides in water and sediment samples collected in the Lourens River catchment was relatively well predicted by the runoff and spray drift transport models applied in estimation of PREX scores (Fig. 3). An overview of the PREX scores per sub-catchment clearly identified sites C and LG4 as the most contaminated sites, with a comparatively
higher number of pesticides falling in the medium to very high categories. In contrast, PREX scores for all pesticides at BB7 and VW were predominantly classified as having medium to very low exposure potential. These broad patterns correspond well with the monitoring data observed in Table 1. Furthermore the indicator identified carbendazim, carbaryl, azinphos-methyl, dimethomorph and methyl-parathion as the pesticides most likely to enter water resources across the catchment. These were the most commonly detected pesticides across all sites.

At BB7 only carbaryl fell into the medium category and was the only pesticide detected in the water phase. Azinphos-methyl and methyl-parathion fell in the low category and were detected a relatively fewer occasions than at C and LG4. While flusilazole fell in the very low category, in comparison to other sites, it had the highest PREX score at BB7 and was detected in the sediment on one occasion. Carbendazim and azinphos-methyl had the highest PREX scores at site C, and, in comparison to other active ingredients for this site, were detected relatively frequently, in water and sediment samples. Methyl parathion, chlorpyrifos and prothiofos had comparatively lower PREX scores, falling in the low to medium categories. Of these active ingredients chlorpyrifos and prothiofos were detected on two and thirteen occasions in the sediment, respectively. Methyl parathion was not detected at this site. Dimethomorph had the lowest PREX score of those active ingredients in the high category and was detected on one occasion in the water phase. Dimethomorph applied in the LG4 sub-catchment scored the highest PREX score for all pesticides included in the index. However, this pesticide was detected on only one occasion in the water phase. Carbendazim also fell in the very high category and was detected on three occasions in water and sediment samples. Carbaryl, methyl parathion and azinphos-methyl also had relatively high PREX scores. Carbendazim and carbaryl were both detected on two occasions at comparatively high maximum concentrations in the water phase, whilst azinphos-methyl (six detections) and methyl-parathion (seven detections) were detected frequently in the sediment phase (methyl parathion was also detected on one occasion in the water phase at a concentration of <0.1 µg L⁻¹). Other active ingredients that were detected in the water phase at this site were chlorpyrifos, prothiofos and trifloxystrobin. These pesticides had comparatively lower PREX scores, falling in the medium and low categories. Prothiofos was however detected more
frequently in the sediment, even more so than azinphos-methyl and methyl-parathion, which scored much higher PREX scores. VW also showed relatively low contamination, with only two detections in the water phase (carbendazim and chlorpyrifos) and a relatively low number of detections in the sediment. All pesticides in this sub-catchment had relatively low PREX scores. Of all the pesticides included in the analysis for site VW, carbendazim and chlorpyrifos had the highest and third highest PREX scores. These pesticides were detected more frequently in the water and sediment phase than any other pesticide applied in this sub-catchment. Azinphos-methyl, with the second highest PREX score was detected on one occasion in the sediment. Site LR had only one pesticide with a PREX score falling in the high category (carbendazim). This pesticide, together with methyl parathion (which was only detected in the sediment phase) was detected most frequently, with three detections in each of the water and sediment phases. Apart from methyl parathion all other pesticides detected at this site were detected less frequently.

### 3.3 Relative Contribution of Runoff and Spray Drift

Assessment of a runoff event in particular is a good measure of the reliability of the model used to predict PELs and subsequent PECs, as runoff events result in the mobilisation of a number of pesticides simultaneously and the level of contamination is dependent on a number of physicochemical and geographical properties. In contrast the variables resulting in contamination from a spray drift event are far less complex and much easier to predict. Assuming that the relative contributions of runoff and spray drift to the PEL from each sub-catchment are accurate (Fig. 4), one would expect pesticides associated with high runoff loss to be present in samples collected from the field during the runoff event on the 15th of November (Table 2).

For site BB7, carbaryl and methyl parathion are both highly associated with runoff activity, accounting for an estimated 84 and 75 %, respectively, of the total PEL when compared to spray drift. Both of these pesticides were detected in samples collected during the runoff event. No pesticides that were predominantly associated with spray drift were detected in collected samples. For site C, of the
pesticides with PREX scores falling in the high category, dimethomorph and carbendazim have the
highest association with runoff activity (94 and 38 %, respectively). Both of these pesticides were
detected in the water phase during the runoff event. Azinphos-methyl and prothifos were also detected
and could be present as a result of sediment mobilised by the runoff event. For Site LG, runoff plays a
major role in the transport of pesticides with high PREX scores. Carbaryl, carbendazim,
dimethomorph and methyl parathion all have high relative runoff contributions to total loss (91, 99, 87
and 96 %, respectively). All four of these pesticides were detected in the water phase during the
runoff event. For Site VW, the overall contribution of runoff to total pesticide losses is relatively low,
with spray drift clearly being estimated as the most important route of pesticide loss. No pesticides
were detected in water or sediment samples during the runoff event. For Site LR, carbaryl and
dimethomorph (88 and 86 %, respectively) and to a lesser extent carbendazim (55 %) all showed
relatively high proportions of runoff contributing to total pesticide loss. All three pesticides were
detected in the water phase during the runoff event.

The ability of the indicator to distinguish between relative runoff and spray drift contributions is
particularly useful with regards to identifying appropriate mitigation measures aimed at minimising
the transport of pesticides into surface waters. For example at site VW, where spray drift is the most
important route of entry, increasing buffer zone width (de Snoo and de Wit, 1998) or the
establishment of vegetative barriers in between the crops and adjacent water body (Reichenberger et
al., 2007) would effectively minimise transport of pesticides into this particular tributary. In contrast,
at site LG4, where runoff is clearly the predominant route of transport, establishment of vegetative
filter strips (Syversen and Bechmann, 2004) or effective drainage of runoff water into a constructed
wetland prior to entry into the tributary (Schulz et al., 2003) could potentially reduce pesticide
concentrations in this particular tributary.

3.4 Pesticide Risk
From a risk perspective, azinphos-methyl and chlorpyrifos posed the highest risk to the aquatic ecosystem (Fig. 5). Sites LG4 and LR have the highest risk associated with pesticide contamination with chlorpyrifos falling in the ‘Very High and ‘High’ categories, respectively and azinphos-methyl falling in the ‘High’ and ‘Medium’ categories, respectively. Site BB7 in particular, appears to have the lowest risk associated with pesticide contamination with all pesticides falling in the ‘Low’ category. VW and LG4 have similar risk profiles with chlorpyrifos falling in the ‘Medium’ category and all other pesticides falling in the ‘Low’ category. The high risk of these pesticides is as a result of their comparatively high toxicity values (Supplementary Data Table S1). Beta-cyfluthrin and cypermethrin both have even higher toxicity (as indicated by their low toxicity concentrations). However both of these pesticides had low transport potential as reflected by their PREX scores. In contrast the majority of other pesticides with very low risk had very low toxicity. Previous research has linked water and sediment associated azinphos-methyl concentrations to negative effects on macroinvertebrate assemblages in the Lourens River catchment (Schulz et al., 2002; Thiere and Schulz, 2004a; Thiere and Schulz, 2004b). Validation of the risk component of the indicator could include a community assessment analysis although it is difficult to distinguish between effects resulting from pesticide contamination and other factors such as sedimentation and habitat modification (Bollmohr and Schulz, 2009).

4. Conclusion

The objective of this paper was to produce an indicator that provides a reliable assessment of the relative exposure and risk of commonly applied pesticides in an agricultural catchment. The outputs of the PREX and PRRI do not represent the absolute exposure and risk but a relative exposure and risk rating among pesticides or land uses in a catchment. It does not take any pesticide interactions or degradation beyond the point of its entry in waterways, (i.e. it provides the “edge of field” scenario). Furthermore the method does not address the mobility and risks of pesticides bound to eroded sediment. Further development of the indicator could focus on incorporating pesticide degradation and sorption dynamics with a simple sediment loss model to estimate pesticide loss via this pathway,
such as in Kookana et al. (2005). It is also important to note that the detection limits of many of the pesticides that were monitored in this study were comparable to the toxicity endpoint derived for the pesticides. In these cases, the absence of detection would not necessarily imply the absence of risk and detailed monitoring campaigns would need to ensure detections limits do not exceed toxicity endpoints for a realistic assessment of risk. Improved detection limits would also significantly enhance the ability to validate the risk indicator more accurately. Finally in cases where SSDs cannot be derived for a pesticide, consideration should be given to applying a safety factor to single species toxicity data (Raimondo et al., 2008).

However, with respect to the Lourens River, the indicator was successful in differentiating between highly contaminated and less contaminated sites, and outputs of the PREX compared relatively well with field based data. A limitation of the validation procedure is that pesticide analysis revealed only the absence or presence of a target pesticide as opposed to a quantitative concentration, which would have been more useful in terms of providing further resolution in differences in contamination between sites. However the methodology adopted here is useful, in that the screening analysis together with the PREX and PPRI indicator allowed for a relatively low cost identification of specific pesticides for more detailed quantitative monitoring in the future. A further advantage of the indicator method described here is that it relies on data input that is easily acquired through freely available databases and GIS tools. In practice the most challenging information to acquire is reliable pesticide application information. These results are important in demonstrating the potential effectiveness of risk indicators, as while many such methodologies have been developed, very few have been validated through field based monitoring. Previous studies in the Lourens River catchment have shown the runoff and spray drift models used in this indicator to be very effective in predicting environmental concentrations of pesticides (Schulz et al., 2001; Dabrowski and Schulz, 2003) and these equations have been used in many indicator methodologies in other southern hemisphere (Kookana et al., 2005) and European (Berenzen et al., 2005) countries in particular. These results therefore contribute to providing increased confidence in the use of these models in this and other risk
indicator applications and, in particular, could therefore lead to improved utilisation of limited resources for monitoring and management in resource constrained countries.

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